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Application of Atmospheric Tracer Techniques for Determining Biogenic Hydrocarbon Fluxes from An Oak Forest

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16. ABSTRACT

The published paper presents the results of an SF_6 tracer release procedure to quantitatively determine the isoprene emission flux for an isolated oak forest in Goldendale, Washington. The paper presents experimental design development to effectively deploy tracer release sites within the forested area to simulate the natural vegetation release. The downwind sample collection program was designed to evaluate several mathematical approaches to calculate isoprene emission flux. The results presented indicate good comparability between the mathematical models and a bag enclosure technique which was also used for isoprene emission flux measurement.

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ABSTRACT

Sulfur hexafluoride tracer was used in a series of experiments to simulate isoprene emissions from an isolated oak forest. The measured tracer release rate and ambient concentrations of isoprene and SF_6 observed along a downwind sample line were combined to determine the mass flux of isoprene from the forest. Results based only upon the maximum isoprene and SF_6 concentrations observed along the downwind sample line were in good agreement with fluxes calculated from the crosswind concentration integrals of isoprene and SF_6. The fluxes determined from the tracer data increased exponentially with temperature and were in close agreement with estimates determined from emission rates measured in a series of branch enclosure samples collected in the forest and a biomass factor taken at the mid-point of a range of available biomass factors. The results of this field study demonstrate the feasibility and usefulness of simulating forest emissions as a tool for investigating turbulent transport in forested areas.

INTRODUCTION

The mass flux of biogenic gases released from a forest have previously been determined using either micrometeorological gradient methods (Knoerr and Mowry, 1981; Quarles, 1981) or vegetation enclosure techniques (Zimmerman, 1981). Although these various approaches yield mass fluxes of similar magnitude, confidence in the results has been limited by uncertainties in the effects of enclosing vegetation, in measurements of small vertical gradients above the forest, and in the applicability of surface-layer theory to non-ideal sites. In many respects, the difficulties involved in measuring mass fluxes from a forest can be avoided by simulating the forest emissions with an inert tracer release and measuring ambient concentrations of the tracer and biogenic gases along downwind sample lines. In this paper, we report the application of this technique to the simplest situation--an isolated forest. Different calculation methods are tested based upon the known tracer release rate and the measured ambient concentrations of the gases, and the results are compared to emission fluxes determined with a vegetation enclosure method. The tracer approach does not require perturbation of the vegetation nor does it rely upon precise gradient measurements. In the present study, the only site requirement is for an isolated source with minimal upwind biogenic gas contributions.

With respect to the more general problem of measuring mass flux from a forest, the present work demonstrates the feasibility of uniquely tagging forest emissions with an inert tracer. Our study also provides data for examining the turbulent transport of gases released from a forest as well as further insight into the magnitude and character of natural hydrocarbon emissions. The latter aspect is of practical value in understanding regional and global atmospheric chemistry.

EXPERIMENTAL PROCEDURES

Fourteen SF_6/isoprene flux experiments were conducted between August 16, and September 28, 1982. Isoprene is the predominate hydrocarbon emitted from oak trees, and, thus, it is the best species to measure in a test of the tracer flux technique. Each tracer test was one hour long and was performed during the afternoon hours when isoprene emissions were high and the winds were the most predictable. Generally two tests were conducted per day. Fourteen branch enclosure samples were collected during the testing period for comparison to the tracer flux experiments.

The study site was located approximately 40 km northwest of Goldendale, Washington, in the south central part of the state. The location is approximately 750 m above sea level with agricultural land on the north and east and range land on the west and south. A deep canyon lies approximately 1 km west of the site and farm lands are beyond the canyon. The forest consists entirely of Oregon white oak (Quercus garryana). Undergrowth beneath the uniform and dense canopy was very sparse consisting mostly of range grass. Summertime meteorological conditions are typically dry and hot; the prevailing winds are from the southwest. An aerial photograph of the test site is shown in Figure 1.

A mechanical weather station on a 2 meter tripod located on the northwest side of the grove was used to determine the average wind speed, direction, and temperature during each test. During most of the tests, additional data were obtained with a modified tethersonde instrument mounted on a 5 m tower located east of the forest. Both meteorological stations were located in an open area approximately 100 meters from the forest, as shown in Figure 2.

A forest inventory to determine the average height of the forest, average number of trees per hectare, average diameter at breast height (cm)

Figure 1. Aerial photograph and topographical map (inset) of the isolated oak forest. Map scale 1:62500 with contour lines in 40 ft. intervals.

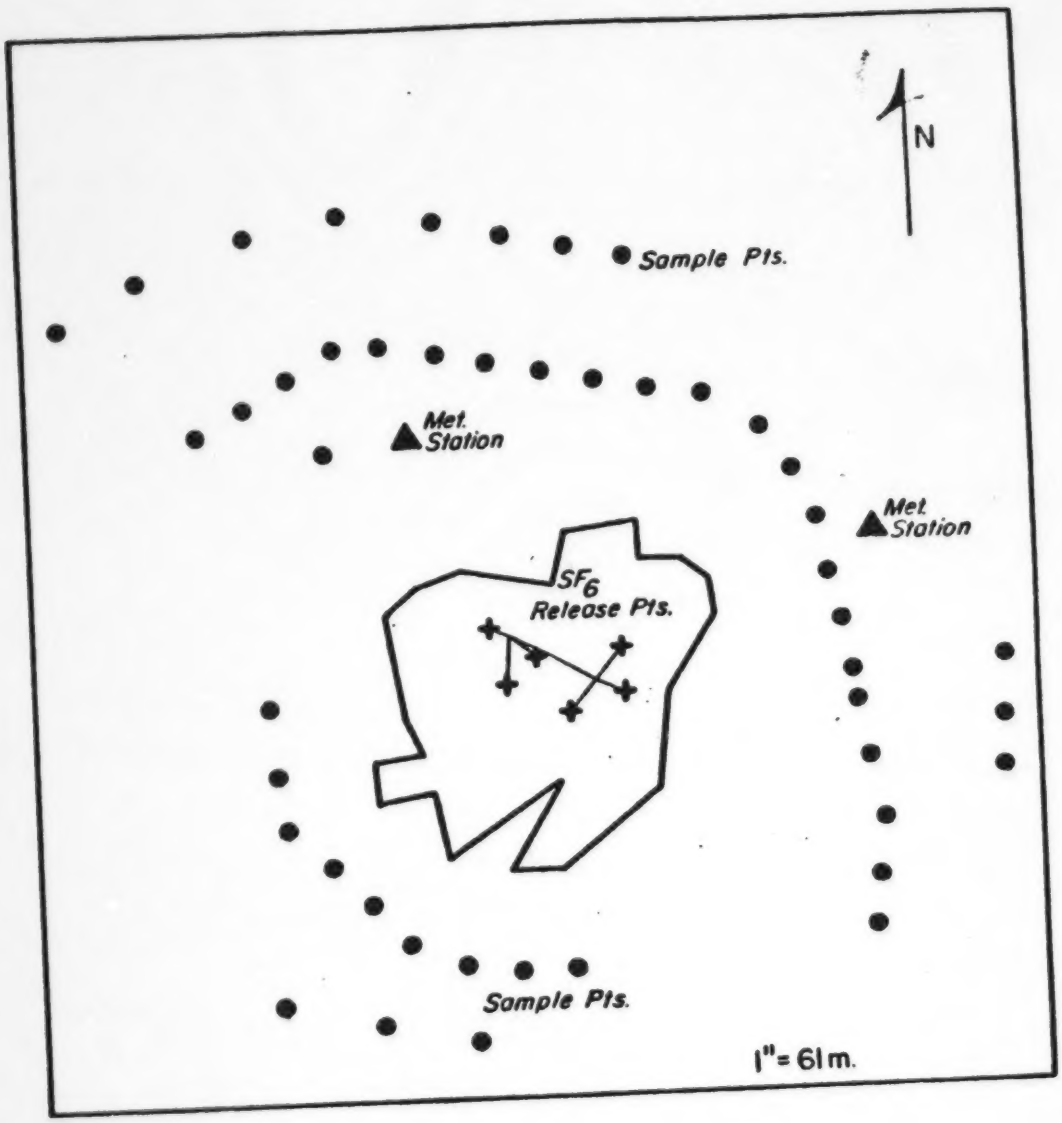

Figure 2. Map of the isolated oak forest showing the SF_6 release points, tracer and hydrocarbon sampling points used during the study, and the locations of the meteorological stations.

and the total area of the grove (hectares) was conducted utilizing simple random sampling. The entire forest area was treated as a single population consisting of ten randomly selected .01 hectare sampling plots. Diameter at breast height (DBH) of each tree and the number of trees were measured in each plot. Simple trigometric measurements with a transit and measuring tape were used to determine the average canopy height. Table 1 summarizes these data.

During each test, sulfur hexafluoride (SF_6) was released for approximately 70 minutes at a constant rate. The SF_6 was contained in a single gas cylinder and released through a pressure regulator and rotameter to a manifold leading through 30 meter lengths of tubing to 6 release points within the forest canopy. A map of the grove with the release points is shown in Figure 2. The release points were positioned approximately 2 meters above the ground. The actual release rate from each point was measured with a bubble flowmeter several times during the release. The measured emission rates from each point are estimated to be accurate within ±5%.

Typically 10 tracer and 8 hydrocarbon samplers were located along a crosswind sample line approximately 100 meters downwind of the grove. A map of all the sampling point locations utilized during the testing period is shown in Figure 2. Portable battery operated samplers (D & S Instruments, Pullman, WA) were used to obtain four sequential 15-minute average tracer samples in 20 cm^3 syringes. Whole air samples for hydrocarbon analyses were also collected at selected points using battery operated Teflon pumps connected to 10-liter Tedlar bags. Each pump and bag was contained in a box to shield them from sunlight. After each test, the contents of the bags were pumped into stainless steel

Table 1. Goldendale Forest Inventory.

Sample Plot	Average Diameter at Breast Height (DBH) (cm)	σ_{DBH} (cm)	No. of Trees
1	15.1	1.31	29
2	14.4	1.64	29
3	15.4	1.64	27
4	13.2	0.96	28
5	12.4	1.07	29
6	13.8	1.05	28
7	15.4	1.10	27
8	14.1	1.25	28
9	15.0	1.11	27
10	12.9	1.56	26

Average DBH for the forest = 14.2 cm
Average trees per hectare = 2800
Average canopy height = 8 m
Total area of the forest = 1.5 hectares

1-liter canisters. SF_6 and hydrocarbon samples collected at the field site were analyzed within 48 hours of collection. A series of stability tests was performed to determine isoprene loss during the period between collection and analysis. It was established that maximum isoprene losses did not exceed 5% over a four day period in either the bags or canisters.

A Hewlett-Packard 5880 gas chromatograph was used for the analysis of isoprene. The chromatograph was equipped with a flame ionization detector and a 30-meter SE-30 glass capillary column. Helium was used as the carrier gas with column flow maintained a 1 cm^3/minute. Separation of isoprene was achieved by temperature programming from -50° to 80°C at 4°C/minute, as shown in Figure 3. To achieve sufficient GC response, a sample concentration step was necessary. A known volume of sample (250-500 cm^3) was drawn through a stainless steel loop partially filled with 60-80 mesh glass beads. The sample loop was immersed in liquid oxygen. Then the trapped hydrocarbons were flushed onto the column by heating the loop with boiling water. Neohexane was used as an external standard for all chromatographic analyses. The results of periodic analyses of the standard were reproducible to within ±5% with an estimated accuracy of ±10%.

Custom-built electron capture gas chromatographs were used to analyze the tracer samples. The analytical system was calibrated during the study by injecting certified standard SF_6 mixtures. The results indicated an accuracy of ±10%. Secondary standard mixtures were analyzed approximately once per hour during the analyses and approximately 15% of the collected samples were reanalyzed with a precision of ±10%.

During each tracer test, branch emission rate samples were collected using the enclosure technique developed by Zimmerman (1981). Figure 4 illustrates the equipment and set-up used to collect branch enclosure samples

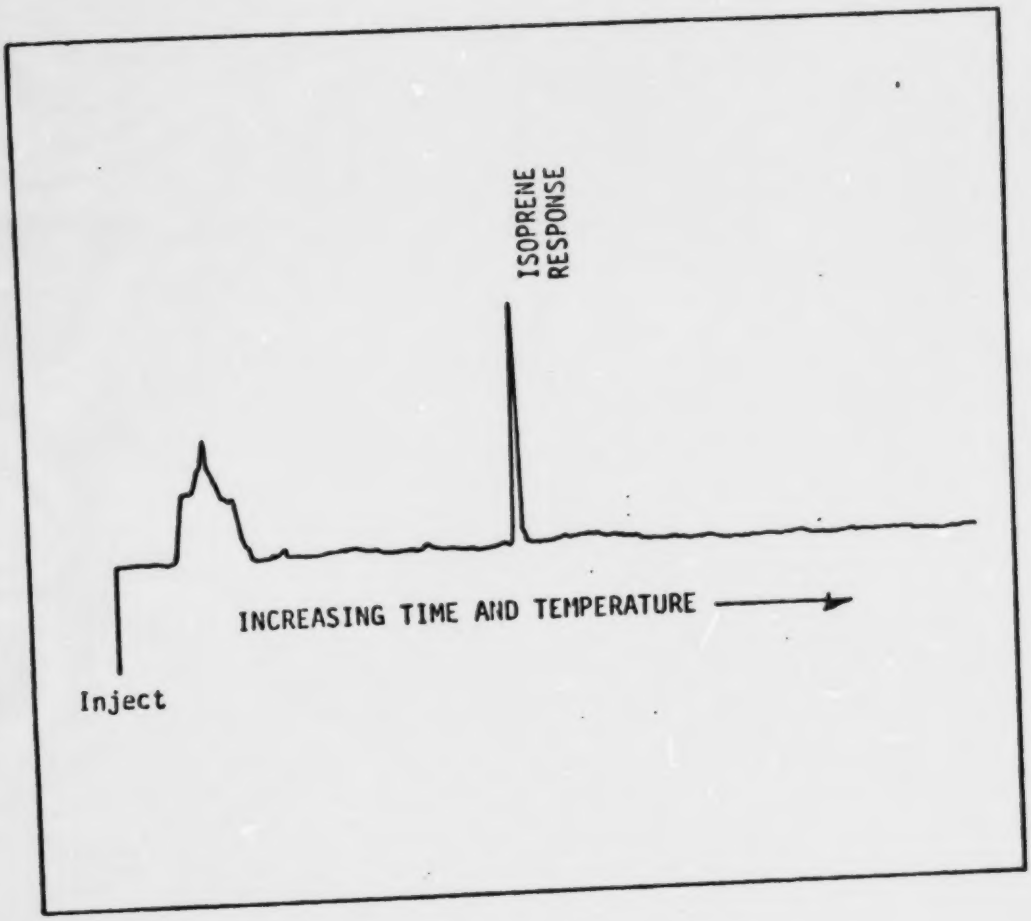

Figure 3. Typical chromatogram from an ambient air sample.

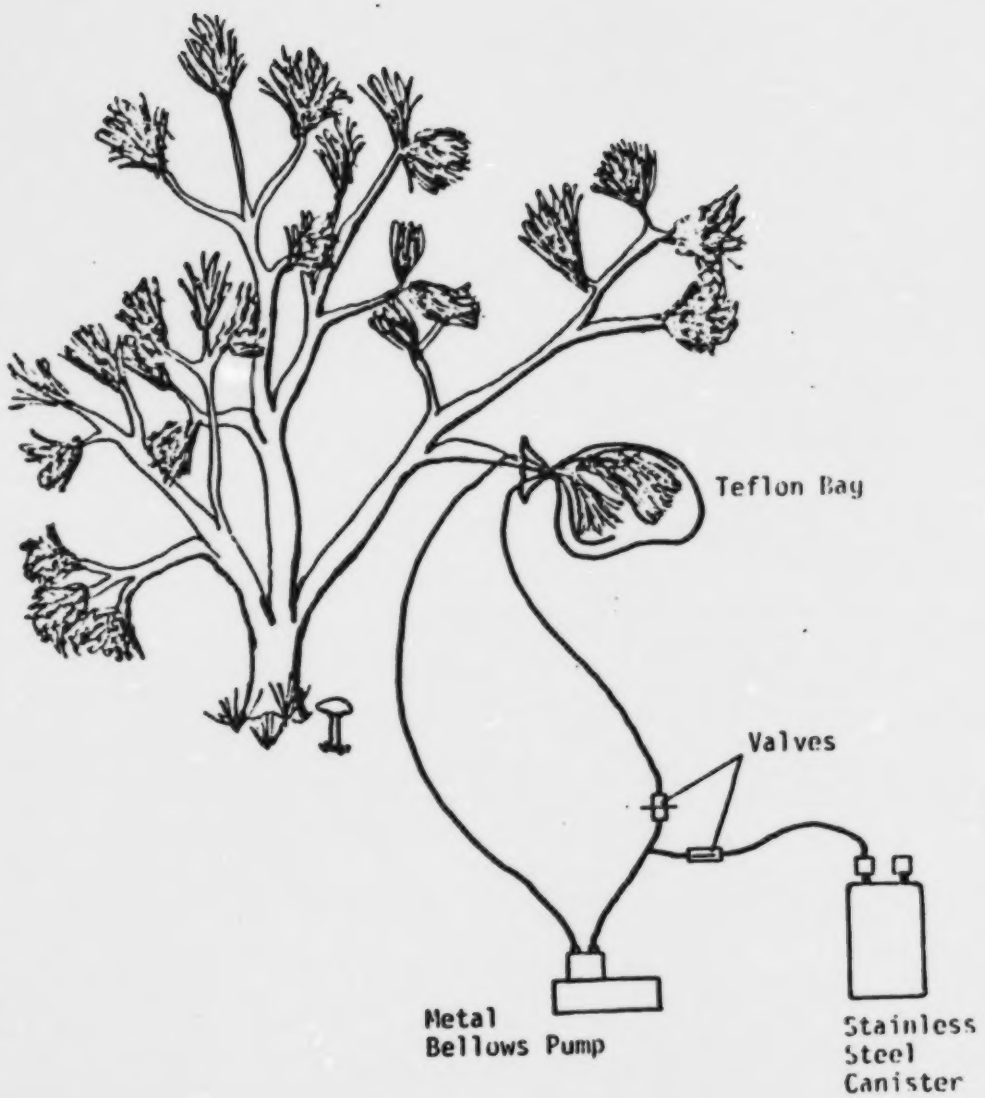

Figure 4. Vegetation enclosure system for measuring isoprene emission rates.

from vegetation. Glass thermometers were used to monitor the temperature inside and outside of the enclosure. In the standard procedure, the thermometer is placed along the branch out of the direct sunlight and two lengths of Teflon tubing are situated along the branch. The Teflon bag is then carefully placed over the branch and sealed by wrapping with Velcro. Immediately after enclosure a background sample is pumped into a 6-liter electropolished stainless steel canister via a battery operated Metal Bellows pump. A known volume and concentration of SF_6 is then injected into the bag in order to determine the enclosure volume. Air is then recirculated through the bag and after a measured amount of time (~6 min) an emission sample is withdrawn from tne bag into another canister. The bag is then removed and the branch clipped and dried to determine the weight of the enclosed leaves. The emission rate is given in terms of micrograms hydrocarbon per gram dry leaf biomass per hour (µg/g-hr):

$$E = \frac{(C_e - C_b)\, V}{(t_e - t_b)\, m}$$

where C_e and C_b are the isoprene concentrations of the emission and background samples, t_e and t_b are the corresponding times of collection, V is the volume of the bag, and m is the dry weight of the branch.

PRESENTATION OF RESULTS AND DISCUSSION

The test conditions during the fourteen tracer flux experiments are listed in Table 2. Temperature varied from 11 to 28°C; wind speeds ranged from 1 to 8.5 m/s; and winds were generally from the southwest. Skies were relatively clear and sunny during all of the tests.

During tests 3, 4, and 14, no isoprene samples were collected downwind of the forest. These experiments will not be included in the remainder of

Table 2. Test Conditions During Tracer Experiments.

Test	Date	Time[a] (PST)	WS (m/s)	WD (deg)	Temp[b] (°C)	SF_6 Flux ($\mu g/m^2$-hr)	C_i-Back[c] ($\mu g/m^3$)	C_i-max[d] ($\mu g/m^3$)	C_{SF_6}-max ($\mu g/m^3$)
1	8/16	1530	5.5	270	26.4	20300	0.8	3.9	4.3
2	8/17	1000	1.0	194	24.4	20600	0.7	1.5	2.5
3	8/17	1330	3.6	260	27.6	no samples			
4	8/31	1330	2.8	228	25.2	no samples			
5	8/31	1600	3.0	217	26.5	17500	1.0	2.0	4.5
6	8/31	1745	3.6	241	23.2	17500	0.9	1.4	6.8
7	9/8	1300	5.8	247	27.0	20300	1.7	4.6	3.5
8	9/8	1500	6.2	240	28.3	20300	1.7	6.5	6.2
9	9/14	1300	7.1	41	15.5	20500	0.2	1.3	4.8
10	9/14	1500	7.9	43	16.0	20500	0.2	1.1	4.9
11	9/22	1300	2.2	145	20.6	19600	0.2	1.4	7.2
12	9/22	1500	3.1	118	21.5	19600	0.3	1.0	4.2
13	9/28	1330	8.5	260	11.1	20800	0.1	0.3	5.2
14	9/28	1500	8.3	257	12.1	no samples			

[a] Start time - tests lasted one hour.

[b] Ambient air temperature.

[c] Upwind isoprene concentrations.

[d] Maximum downwind isoprene concentrations minus upwind.

the discussion. Tests 9 and 10 were conducted on the south side of the grove with strong northeasterly winds. The sample line during tests 9 and 10 was located approximately 30 meters from the edge of the forest. The crosswind profiles from these tests indicated that three individual SF_6 plumes were present. This suggests the tracer was not thoroughly mixed before crossing the sample line and thus the forest emissions were not accurately simulated. For this reason, the results from tests 9 and 10 are not included in the following calculations.

Tests 1, 2, 7, 8, and 13 showed similar broad plumes of isoprene and tracer with maximum concentrations very nearly co-located along the downwind sample line. During tests 6, 11, and 12 the downwind sample line encompassed slightly more than half of the tracer and isoprene plumes, while in test 5 the sample line contained less than half of the isoprene and SF_6 plumes. A typical example for each case is shown in Figure 5.

Background concentrations of isoprene measured upwind of the forest during each test ranged from approximately 0.1 to 1.7 $\mu g/m^3$ as indicated in Table 2. These concentrations were exponentially correlated with ambient temperature ($r=0.94$). Maximum isoprene concentrations attributed to the isolated forest (observed minus background) varied between 1.0 and 6.5 $\mu g/m^3$, and the maximum concentrations were also exponentially correlated with temperature ($r=0.87$). Maximum SF_6 concentrations were between 2.5 and 7.2 $\mu g/m^3$, but these values were not correlated with temperature. As a result, it appears that the variation of isoprene concentrations with temperature was related to variations in source strength and not to changes associated with atmospheric stability and dilution rates. Lamb et al. (1983) also observed an exponential relationship between isoprene concentrations measured 6 m above a Pennsylvania oak forest and ambient temperature.

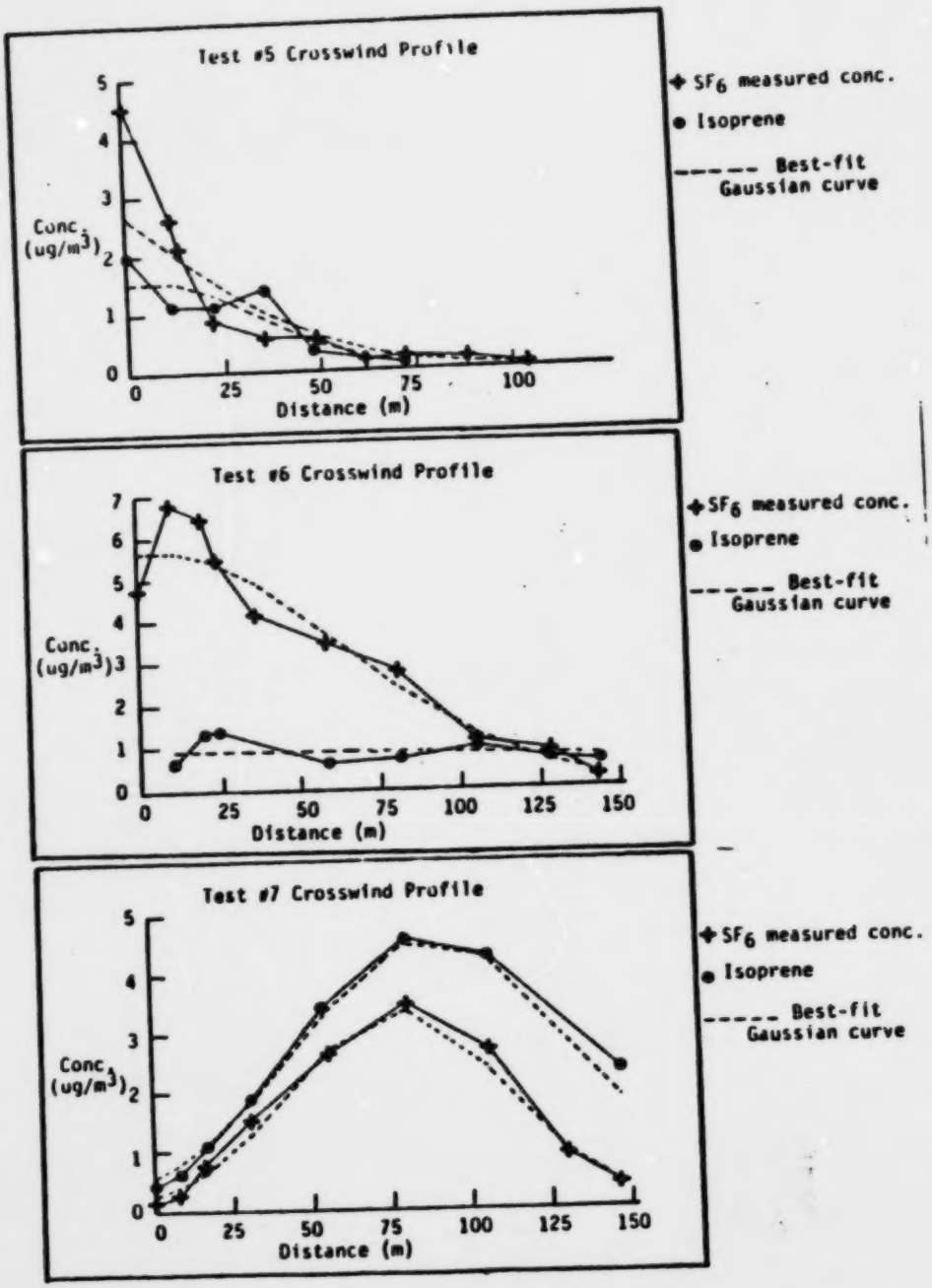

Figure 5. Typical crosswind tracer and isoprene concentration profiles with best-fit Gaussian curves.

The slope and correlation coefficient calculated from the Pennsylvania data were quite close to those for the present study; however, the isoprene concentrations observed in Pennsylvania varied between 3.0 and 15 $\mu g/m^3$.

Two different methods were used to calculate isoprene emission fluxes based upon the known tracer release rate and measured ambient concentrations of isoprene and SF_6. In each case, it was assumed that isoprene was conserved during transport. This assumption is reasonable for the short travel distances used in the tracer experiments. Chemical lifetimes for isoprene reactions with ozone and hydroxyl radical range from 1.3 to 34 hours depending upon ambient ozone and hydroxyl concentrations (Altshuller, 1982). For the conditions observed in these tests, the maximum transport time from the forest to the sample line was much less than 0.1 hours which is far less than the reported lifetimes.

If the SF_6 emissions accurately simulate all of the isoprene emissions, then the ratio of the isoprene and SF_6 concentrations observed downwind will equal the corresponding ratio of the emission fluxes. However as shown in the crosswind profiles in Figure 5, the widths of the SF_6 and isoprene plumes were typically not identical, and in some cases, the plumes were offset horizontally. For these reasons, the simplest method for calculating the flux of isoprene is to consider only the ratio of the observed maximum isoprene and SF_6 concentrations:

$$F_i = F_{SF_6} \cdot \frac{C_i(max)}{C_{SF_6}(max)} \qquad (1)$$

where F_i is the calculated isoprene flux ($\mu g/m^2$-hr), F_{SF_6} is the measured tracer flux ($\mu g/m^2 hr$), $C_i(max)$ is the isoprene maximum concentration, and $C_{SF_6}(max)$ is the maximum tracer concentration observed along the sample line.

In the cases where the horizontal distributions of SF_6 emissions are slightly wider than and possibly offset from the isoprene emission distributions, the calculations can be improved by considering the ratio of the crosswind integrals.

$$F_i = F_{SF_6} \frac{\int_{-\infty}^{\infty} C_i \, dy}{\int_{-\infty}^{\infty} C_{SF_6} dy} \qquad (2)$$

where $\int_{-\infty}^{\infty} C_i(y)dy$ is the crosswind integral of the downwind isoprene concentrations and $\int_{-\infty}^{\infty} C_{SF_6}(y)dy$ is the crosswind integral of the SF_6 concentrations. In this approach, it is assumed that the vertical dispersion rates for both gases are equal.

The crosswind integrals of SF_6 and isoprene for use in (2) were determined by direct integration of measured concentrations and also by integration of the best-fit Gaussian curve through the measured observations. In both instances, the position of the sample points were projected onto the line normal to the mean wind direction and the concentration profiles were integrated using trapezoidal integration. In almost all tests, the observed concentration profiles were Gaussian in appearance, but in several instances the measured profile did not encompass the entire SF_6 or isoprene plume. By employing best-fit curves to the data, the profile of the entire plume can be obtained and integration errors associated with chopping off a portion of the plume are eliminated. The approach for calculating best-fit Gaussian curves was initially developed to perform tracer mass balances in tracer dispersion studies and is described in detail elsewhere (Lamb, 1978; Sackinger et al., 1982). The use of best-fit Gaussian curves does not imply application of the common Gaussian plume model; rather the use of the curves only takes advantage of the Gaussian shape of the observed concentration profiles.

Before proceeding with the presentation of results, it is worthwhile considering the origin of eq. (2). The total emission rate of isoprene (μg/s) can be calculated directly from a mass balance expression:

$$Q_i = \int_0^{\infty} \int_{-\infty}^{\infty} u(z)\, C_i(y,z)\,dy\,dz \qquad (3)$$

where $u(z)$ is the vertical wind speed profile and $C_i(y,z)$ is the concentration distribution of isoprene in a vertical plane normal to the mean wind direction at some distance downwind of the source. Because vertical profiles of wind speed and concentration were not measured during the study, application of (3) requires assumptions concerning the vertical profiles of wind and concentration. One approach is to assume a power law wind speed profile:

$$u(z) = u_r(z/z_r)^p \qquad (4)$$

where u_r is the wind speed measured at a reference height z_r and p is an empirical stability coefficient (normally equal to .25 for near neutral conditions). A Gaussian vertical concentration distribution can also be assumed:

$$C(y,z) = \overline{C}_i(y,z_r)\left\{\frac{\exp\left[-\frac{1}{2}\left(\frac{H+z}{\sigma_z}\right)^2\right] + \exp\left[-\frac{1}{2}\left(\frac{H-z}{\sigma_z}\right)^2\right]}{\exp\left[-\frac{1}{2}\left(\frac{H+z_r}{\sigma_z}\right)^2\right] + \exp\left[-\frac{1}{2}\left(\frac{H-z_r}{\sigma_z}\right)^2\right]}\right\} \qquad (5)$$

where $\overline{C}_i(y,z_r)$ is the isoprene crosswind integral at ground-level, H is the effective source height, and σ_z is the vertical diffusion coefficient.

Values of σ_z can be obtained in an iterative approach using (3), (4), and (5) with the crosswind integral of the tracer concentrations and the measured tracer emission rate. It is in this step that we assume that the tracer and isoprene are vertically dispersed at the same rate. As a result,

it is not necessary to obtain detailed vertical profiles of wind speed or concentration. It can be shown, however, that this assumption leads directly to (2). For example, if the simple assumption is made that wind speed is constant with height and that the concentrations of tracer and isoprene were uniformly mixed in the vertical over a height L, then the mass balance expression for isoprene becomes:

$$Q_i = uL \int_{-\infty}^{\infty} C_i(y)dy \qquad (6)$$

where the product uL is obtained from the SF_6 data:

$$uL = \frac{Q_{SF_6}}{\int_{-\infty}^{\infty} C_{SF_6}(y)\, dy} \qquad (7)$$

Substitution of (7) into (6) yields the ratio of concentration integrals multiplied by the tracer release rate as given in (2).

Still another method for estimating isoprene emission rates from a forest is to calibrate an atmospheric dispersion model for the existing conditions using the SF_6 data and then apply the model to isoprene transport to determine the best estimate of the emission flux. Arnts et al. (1981) employed the Point Area, Line Source (PAL) Gaussian algorithm to estimate alpha-pinene flux from a loblolly pine forest. Tracer data were used to define the best Pasquill-Gifford dispersion curves for the test conditions. However, application of a simple Gaussian Plume model in the present case does not appear to provide any unique or improved results, and this modeling approach will not be tested with the data from the isolated forest.

Isoprene fluxes calculated with (1) and (2) are shown in Figure 6a-c. The fluxes determined from the ratio of the maximum concentrations range from 1200 to 26600 $\mu g/m^2$-hr with an average flux of 11000 $\mu g/m^2$-hr. Fluxes calculated with the ratio of the observed crosswind concentration integrals

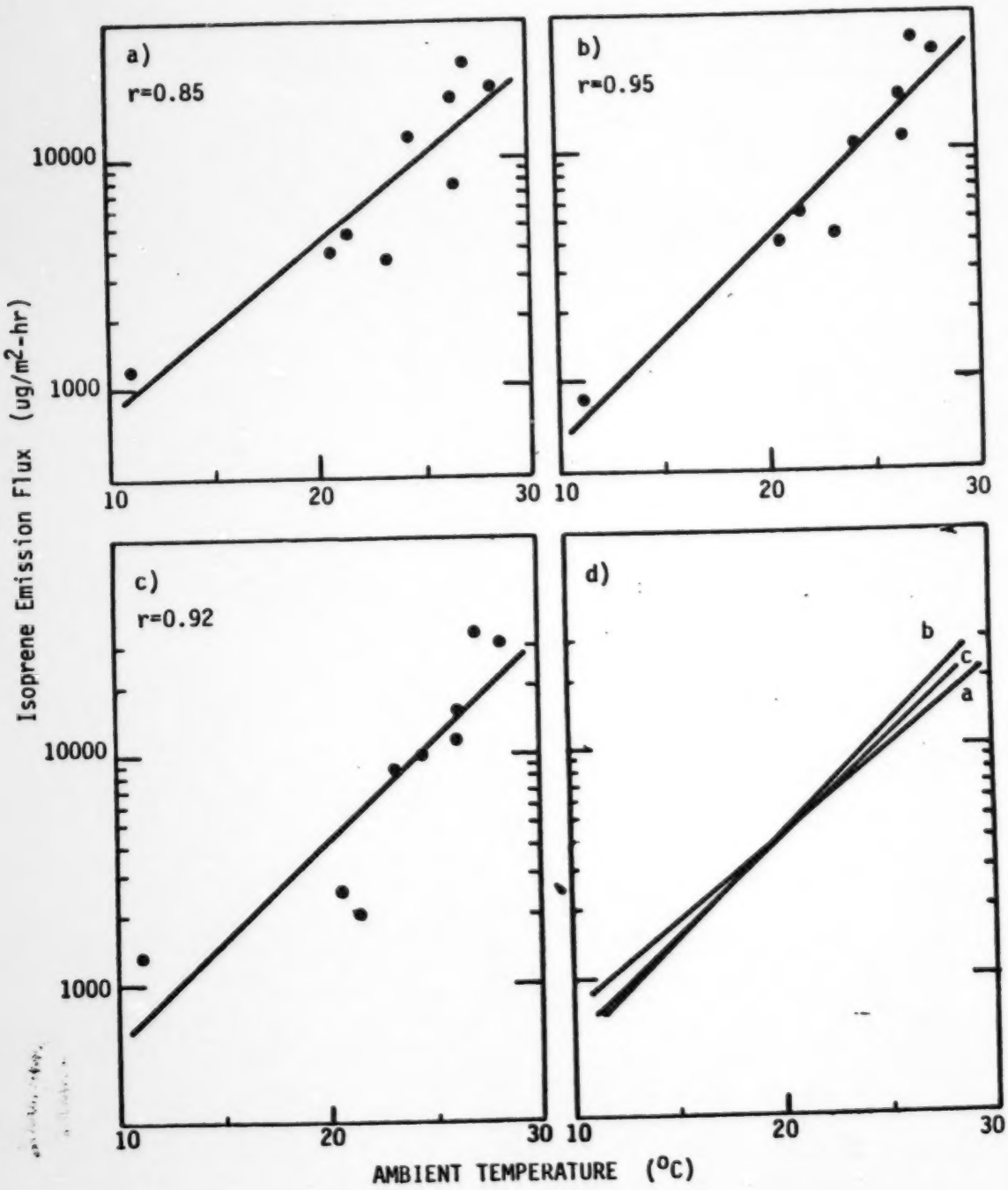

Figure 6. Isoprene flux vs. ambient temperature: a) from the ratio of the observed maximum isoprene and SF_6 concentrations; b) from the ratio of the observed isoprene and SF_6 crosswind integrals; c) from the ratio of the Gaussian best-fit isoprene and SF_6 crosswind integrals; and d) comparison of lines a-c.

vary from 840 to 31000 $\mu g/m^2$-hr with a mean flux of 12500 $\mu g/m^2$-hr. Fluxes determined from the ratio of the best-fit crosswind concentration integrals increase from 1300 to 35700 $\mu g/m^2$-hr with an average flux of 13400 $\mu g/m^2$-hr. The range and mean of the calculated fluxes were lowest for the ratio of the maximum concentrations and highest for the ratio of the best-fit concentration integrals. Since there were fewer hydrocarbon sample points than tracer sample points, the probability for measuring the true maximum concentration was lower for isoprene than for SF_6. With respect to the differences between the fluxes based upon observed and best-fit profiles, the results indicate that extension of the plume profiles via the best-fit procedure increased the integrals of the isoprene profiles relative to the integrals of the SF_6 concentrations.

The strong dependence of isoprene emission rates upon temperature has been well documented (Flykt, 1979; Tingey et al., 1978; and Lamb et al., 1983). As a result, the degree of correlation between the estimated fluxes and temperature can be used as a basis of comparison of the different calculation methods. In each procedure, the results in Figure 6a-c exhibit a positive exponential relationship between isoprene flux and ambient temperature as was observed for the ambient isoprene concentrations. The correlation coefficient for the calculations based upon the ratio of the maximum concentrations was 0.85 which is slightly less than the correlation coefficients based upon the ratio of the integrals of observed (r=0.95) and best-fit (r=0.92) concentration profiles.

The three different regression lines are graphed together in Figure 6d. Generally, all of the procedures yield very similar estimates of the isoprene flux. The reasonable agreement between the first method based upon only the maximum concentrations and the two integral methods indicates that the tracer

emission system was a good simulation of horizontal distribution of the forest emissions. It should also be noted that the tracer and isoprene maximum concentrations were co-located in 6 tests, and the maximum locations for the two gases were offset by only 1 sample point in all of the other tests.

The consistency achieved with the different calculation methods is one indication that the tracer simulation was valid. As a second test of the procedure, isoprene emission rates were measured directly with the branch enclosure technique. Data for the fourteen vegetation enclosure samples obtained during the testing period are summarized in Table 3. Excluding one sample collected in direct sunlight where heat buildup in the bag was excessive, isoprene emission rates varied from .41 μg/g-hr to 130 μg/g-hr with 70% of the samples between .4 to 6 μg/g-hr. The median emission rate was 4 μg/g-hr.

In order to use the individual branch emission rates measured by the enclosure method to predict emission fluxes, a biomass factor (g/m^2) must be determined for the forest. Algorithms have been developed for various tree species which can be used to estimate the amount of biomass per square meter given the average value of the tree diameter at breast height. Although no algorithm has been reported for Oregon white oak, biomass relationships do exist for other hardwood species. Monk et al. (1970) developed a relationship from an oak-hickory forest in Georgia. They sampled 23 trees ranging from 2.8 to 36 cm in diameter. Reiners (1972) collected samples from an oak forest consisting primarily of white and northern pin oaks in Minnesota. Another relationship was reported by Sollins et al. (1973) from 40 coniferous and deciduous species in the southeastern United States. A fourth relationship was developed by Whittaker et al. (1974) from 3 deciduous tree species in

Table 3. Isoprene Emission Rates from Branch Enclosure Samples.

Sample	Time (PST)	Date 1982	Ambient Temperature (°C)	Enclosure Temperature (°C)	Emission Rate (µg/g-hr)
1	1220	8/17	27.2	33	130
2	1410	8/31	25.0	24	94
3	1606	8/31	26.7	28	300*
4	1818	8/31	23.9	22	0.9
5	0843	9/8	19.0	19	1.1
6	1309	9/8	27.7	29	36
7	1525	9/8	28.3	33	110
8	0924	9/14	10.0	11	0.4
9	1235	9/14	13.3	15	4.0
10	1451	9/14	14.4	18	8.0
11	1034	9/22	16.7	19	0.8
12	1524	9/22	21.7	24	2.6
13	1544	9/22	21.7	22	1.2
14	1343	9/28	11.1	16	7.3

* sampled in direct sunlight

New Hampshire. The 4 biomass relationships and the respective biomass factors for the isolated oak forest are presented in Table 4. The biomass factors range from 574 to 1033 g/m^2.

The emission fluxes calculated from the branch enclosure method with the minimum and maximum biomass factors are plotted versus temperature in Figure 7 along with the results from the tracer flux experiments using eq. (2) and the observed concentration integrals. The branch enclosure results show the same type of positive exponential relationship (r=0.62) betweeen emission flux and temperature as the tracer data. At 30°C ambient, emission fluxes for the different biomass factors range between 24500 and 44100 $\mu g/m^2$-hr with a mid-point flux of 34300 $\mu g/m^2$-hr. The biomass factor corresponding to the mid-point flux equals 804 g/m^2. The flux estimated for the tracer technique at 30° equals 32500 $\mu g/m^2$-hr. The regression lines based upon these two sets of data also have essentially identical slopes. Using the isoprene flux calculated with the mid-point of the biomass factors as a basis for comparison, the tracer method and branch enclosure technique agree within 6% at all temperatures.

The excellent agreement between the slopes of the lines from the tracer and enclosure data is another indication that the emission flux estimates from both procedures are valid. Although the actual biomass factor is uncertain, the range of factors yields flux estimates which bracket the flux determined from the tracer data. In fact, the close agreement obtained for the mid-point biomass factor suggests that the correct biomass factor is approximately 800 g/m^2.

To further evaluate the tracer method, isoprene emission rates reported in other studies using non-tracer procedures were compared with results obtained by this study. These data are summarized in Table 5. A biomass

Table 4. Biomass Algorithms and Estimated Biomass Factors

Source	Forest Type	Location	Biomass Algorithm $L = a(DBH)^b$ a (g/tree)	b (1/cm)	Biomass Factor[1] (g/m^2)
Monk et al. (1970)	oak-hickory	Georgia	9.1	2.19	842
Reiners (1972)	oak	Minnesota	29.3	1.67	687
Sollins et al. (1973)	deciduous and coniferous species	southeastern U.S.	41.1	1.70	1033
Whittaker et al. (1979)	deciduous species	New Hampshire	14.5	1.87	574

[1] DBH = 14.2 cm with 2800 trees/hectare (see Table 1).

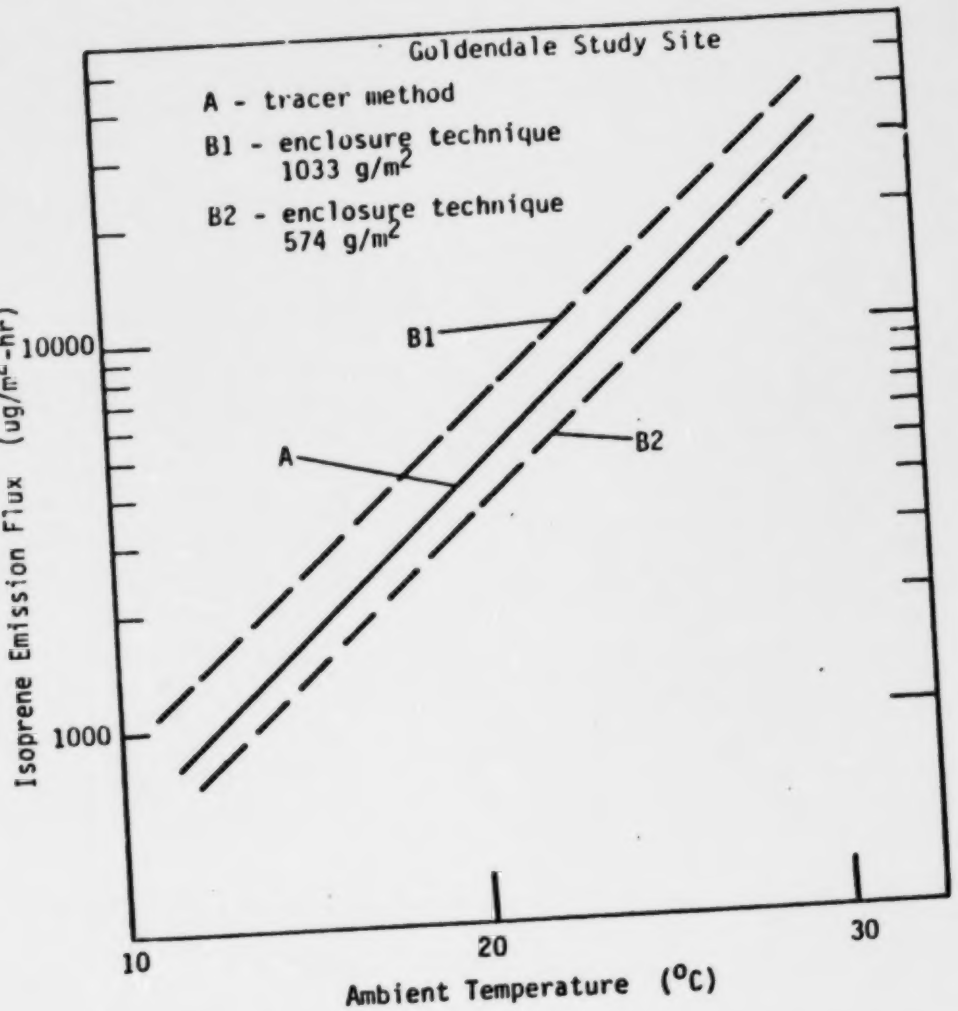

Figure 7. Comparison of isoprene emission flux vs. temperature determined from the tracer and enclosure procedures.

Table 5. Comparison of Isoprene Emission Rates from Various Field and Laboratory Studies

Investigator	Species Sampled	Sample Method	Isoprene Emission Rate @ 30°C (μg/g-hr)	Flux[a] ($\mu g/m^2$-hr)
Flyckt (1979)	red oak, Pullman Washington	Branch Enclosure Method	38.9	31300
Lamb et al. (1983)	5 hardwood species, Pennsylvania	Branch Enclosure Method	27.5	22100
Lamb et al. (1983)	oak-hickory forest, Pennsylvania	Aerodynamic Method	30.7	24700
Goldendale Study	Oregon white oak, Goldendale, WA.	Tracer Method	40.5	32600
Goldendale Study	Oregon white oak, Goldendale, WA.	Branch Enclosure Method	42.7	34300
Zimmerman (1977)	oak species	Branch Enclosure Method	24.7	19900
Tingey et al. (1978)	live oak	Laboratory Growth Chamber	33.0	26500

[a] flux calculated using a biomass factor of 804 g/m^2

factor of 804 g/m^2 was used for comparison purposes to calculate the emission fluxes from the emission rates reported in each study. It should be emphasized the these isoprene fluxes are calculated for a variety of hardwood species, in various locations, and under different soil and environmental conditions. The estimated isoprene emission fluxes range from 19900 to 34300 $\mu g/m^2$-hr at 30°C.

The differences among the studies that are indicated in Table 5 may be related to differences between the estimated biomass factor at the isolated forest and the true biomass factors for the other forests or to differences in the inherent isoprene emission rates from different hardwood species. However, the magnitude and range of emission fluxes at the Goldendale site determined by the tracer method are reasonably similar to those determined in the other studies. Our results represent good evidence for the reliability of reported biogenic hydrocarbon emission rates.

A significant aspect of the present study is the direct establishment --- through use of the tracer data --- of the role of atmospheric dilution in the occurrence of low ambient isoprene concentrations. As previously indicated, the range and magnitude of the isoprene emission rates and fluxes determined in this work are quite similar to the rates and fluxes obtained in other locations. At the same time, the ambient concentrations of isoprene measured downwind of the oak forest are also quite comparable to ambient isoprene concentrations reported for other locations. For example, in the present work, the emission fluxes varied from 840 to 31000 $\mu g/m^2$-hr, the emission rates ranged from 1 to 40 $\mu g/m^2$-hr, and the maximum ambient concentrations measured downwind of the oak forest were between 0.3 and 6.5 $\mu g/m^3$. In comparison, Holdren et al. (1979) measured biogenic hydrocarbon concentrations in the range 0.1 to 4 $\mu g/m^3$ beneath the canopy of

a fir forest and measured an emission flux of 3100 $\mu g/m^2$-hr. In the Pennsylvania work by Lamb et al. (1983), isoprene concentrations in the range of 3 to 15 $\mu g/m^3$ were observed 6 m above the canopy and emission fluxes from 2500 to 16000 $\mu g/m^2$-hr were determined. Zimmerman (1979) measured an emission rate for one live oak branch of 29 $\mu g/g$-hr. He collected an ambient air sample close to the branch which contained an isoprene concentration of 2.5 $\mu g/m^3$. Westberg and Lamb (1983) reported nonmethane hydrocarbons (NMHC) concentrations at 4 sites in and around Atlanta, Georgia. They found a mean NMHC concentration of 476 ppbC of which 1% was determined to be isoprene (2.7 $\mu g/m^3$). Cronn et al. 1978 collected air samples within the Great Smoky Mountain National park in Tennessee. They reported an average ambient isoprene concentration of 3.4 $\mu g/m^3$ and a maximum concentration of 10 $\mu g/m^3$.

Since the levels of isoprene measured at Goldendale were entirely associated with dilution of the forest emissions, the reasonable agreement of these concentrations with those observed elsewhere suggest that atmospheric dilution of gases released from very diffuse sources can have a dominant effect upon the resulting ambient concentrations. Previous discussions of the relative magnitudes of biogenic and anthropogenic emission inventories have seldom accounted for the effects of differences in diffuse and concentrated sources. The results presented here demonstrate that low ambient air concentrations of biogenic gases do not necessarily imply low source strengths or high chemical reactivity.

SUMMARY AND CONCLUSIONS

The simulation of isoprene emissions from an isolated forest of Oregon white oak with a multi-point SF_6 tracer release provided a straightforward method for determining the isoprene emission flux. Results from a series of tracer experiments indicated that the forest emissions could be adequately simulated with 6 tracer release points in the forest. Isoprene emission fluxes calculated from the measured tracer release rate and the ratio of the maximum isoprene and SF_6 concentrations observed along a downwind sample line were in good agreement with fluxes estimated using the ratio of the crosswind integrals of isoprene and SF_6 concentrations. Results from both calculation procedures were exponentially correlated ($r \geq 0.85$) with ambient temperature. These emission fluxes also agreed within 6% with measurements of isoprene emission fluxes obtained with a vegetation enclosure technique. The fluxes determined with the enclosure procedure were based upon a biomass factor at the mid-point of a range of four available biomass algorithms reported for other deciduous forests. Emission rates from this work were also similar in magnitude to those reported for other isoprene-emitting hardwoods.

The ambient background and maximum isoprene concentrations observed during the tracer experiments increased exponentially with ambient temperature over the range 0.1 to 6.5 $\mu g/m^2$. This range of isoprene concentrations is essentially the same as reported by a number of other investigators for a variety of locations. The isoprene and tracer data together underscore the importance of atmospheric dilution in the production of low ambient concentrations of biogenic hydrocarbons emitted from forested areas.

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